

Some Aspects of the Fully Soluble Efficient Vulcanisation (FSEV) System

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The paper briefly discusses the development of the fully soluble efficient vulcanisation system. Its cure characteristics and advantages over the conventional vulcanising system are compared and structural features of the vulcanisate networks are also examined in relation to physical properties. Heat ageing and its protection by antidegradants together with technological properties of carbon black-filled rubbers of the fully soluble efficient vulcanisation system are evaluated and shown to be fully satisfactory.

In many uses of rubber, natural rubber (NR) is preferred to its synthetic analogue, *cis* 1-4 polyisoprene because NR is highly resilient, has good strength and heat build-up characteristics. These properties are achieved by using curing systems containing two to three parts per hundred rubber (phr) of sulphur and 0.5–1.0 phr of an accelerator.

The conventional system (high sulphur/low accelerator) shows excellent initial physical properties which slowly deteriorate with service life. This slow deterioration of some properties with service life is satisfactory for most applications, but in applications such as in engineering products where high precision and low creep properties over the entire service life of a rubber article are required, the conventional system is inadequate. This is due to the high concentration of sulphur and low concentration of accelerator in the system giving rise to vulcanisates which contain mainly polysulphidic crosslinks. These crosslinks are known to be deficient in heat ageing, creep and permanent set (BATEMAN *et al.*, 1963). The earlier generation of so-called efficient vulcanisation (EV) systems (SKINNER AND WATSON, 1967), in which a high concentration of accelerator is used, are still inadequate for the engineering applications because of their poor strength especially at high temperatures and the low fatigue life.

It was speculated at that stage of development of vulcanisation chemistry that the non-network materials and post-vulcanisation products could contribute to these adverse properties. In fact, it was later shown that it was the zinc carboxylate (zinc soap of fatty acid) which has an adverse effect on creep and stress relaxation properties (HOLLEY AND SMITH, 1973). The pursuit of this study and its understanding resulted in the concept of soluble compounding and the fully soluble efficient vulcanisation (FSEV) system (CHAN, 1974).

In the FSEV system, a minimum concentration of sulphur is used in order to achieve maximum solubility in rubber. The stearic acid is replaced by 2-ethyl hexanoic acid or its zinc soap; 2-morpholinyl-benzothiazyl sulphenamides (MOR) replaces cyclohexylbenzothiazyl sulphenamides (CBS) and a more soluble tetra-butyl thiuram disulphide replaces tetramethyl thiuram disulphide as accelerator. The mix formulation of the FSEV system, under normal mixing cycles, gives rise to a more uniform dispersion of curatives with the final physical properties of rubber vulcanisates being more reproducible.

CURE CHARACTERISTICS

The vulcanisation characteristics of the different curing systems are shown in *Figure 1*.

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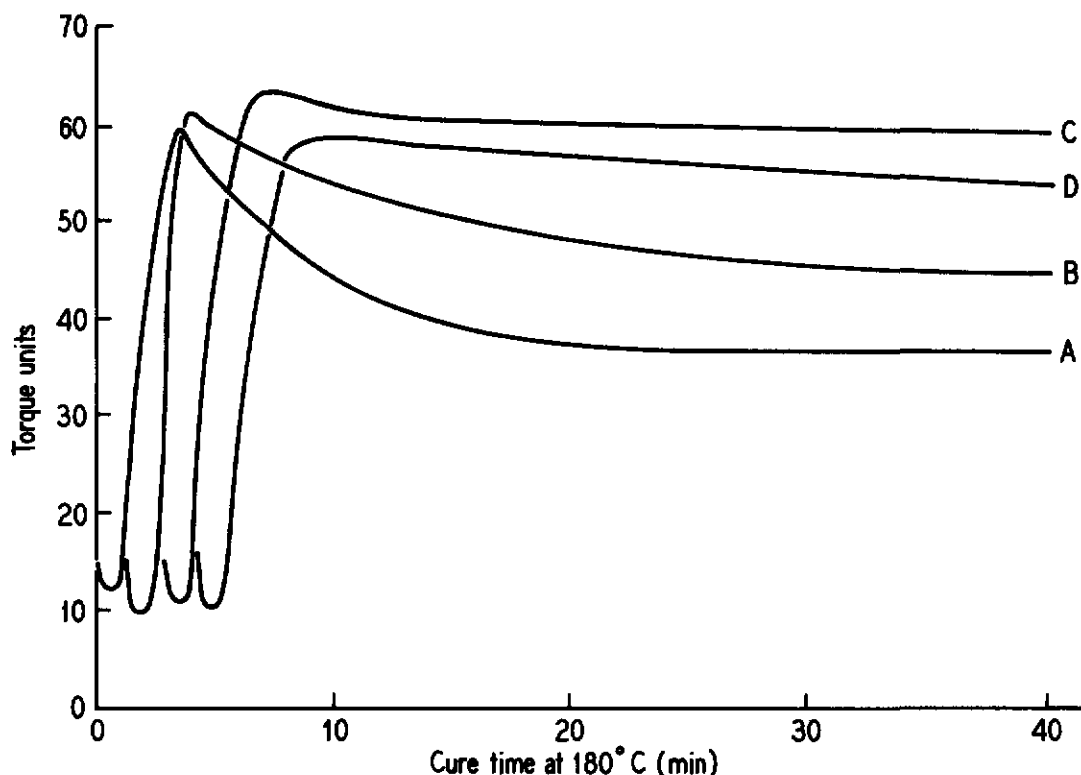


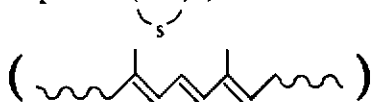
Figure 1. Effect of vulcanising system on reversion. Monsanto rheometric traces at 180°C of DPNR with 50 phr FEF black and: A, Conventional high sulphur system (S, 2.5, CBS, 0.5); B, Semi-E.V. system (S 1.2; CBS, 1.8), C, EV system (S, 0.25; MOR, 2.1; TMTD, 1.0); D, FSEV (S, 0.8; TBTD, 0.8; MOR, 1.96). All curves start at zero time: they are offset to emphasise their differences.

The FSEV system is compared with a semi-EV, a conventional and an EV system. The results show that the FSEV system has the overall advantage of better resistance to curing reversion when compared with the conventional and semi-EV systems. Its scorch behaviour is adequate to provide good processability which is exemplified by its application in high temperature injection moulding and vulcanisation (WHEELANS, 1974). Modulus reversion of 5% in a FEF black filled compound is reached only after at least 4.5 h at 140°C, 75 min at 160°C and about 5 min at 180°C. Thus, the resistance to reversion is four to eight times longer than the conventional system at these vulcanisation temperatures.

NETWORK STRUCTURAL CHARACTERISTICS

Chemical treatments and analyses of network structural features are well established (SAVILLE AND WATSON, 1967). They include triphenylphosphine treatment (MOORE AND TREGO, 1964), selective scission of sulphidic crosslinks (CAMPBELL, 1969), radioactive tracer analyses of accelerator pendent groups (CAMPBELL, 1970; PARK *et al.*, 1972) and instrumental analyses for alkenes (PORTER AND HIGGINS, 1963). The network structural features characterised by the use of these techniques are mono-sulphidic crosslinks (R-S-R), disulphidic crosslinks (R-S-S-R), polysulphidic crosslinks (R-S-S_x-S-R, $x \geq 1$), accelerator pendent

groups (R-S-X, X = accelerator fragment), cyclic sulphides (R-R)⁴, trienes



and dienes



These are schematically represented in Figure 2. The composition of these features in a given vulcanisate depends on the type of curing system.

The typical FSEV recipe cured at 140°C shows maximum total chemical crosslinks (maximum modulus in the physical sense) at a cure time of 90 minutes. The maximum does not then vary significantly up to a cure time of 360 minutes. At the optimum cure time, the network structural composition consists of 20% polysulphidic crosslinks, 30% disulphidic crosslinks and 50% monosulphidic crosslinks. This composition changes with cure time. At a cure time of 360 min, it has 5% polysulphidic crosslinks, 25% disulphidic crosslinks and 70% monosulphidic crosslinks. The corresponding sulphur vulcanisation efficiency, E-value, (SAVILLE AND WAT-

SON, 1967) at these cure times has been reduced from 5.8₇ to 4.1₃, and the E'-value (after triphenylphosphine treatment) (MOORE AND TREGO, 1964) changes from 4.0₂ to 3.8₂. These results show that with the prolonged curing beyond the optimum cure time the polysulphidic crosslinks and, to a lesser extent, the disulphidic crosslinks have been desulphurated to form more stable monosulphidic crosslinks. Some thermal decomposition of polysulphidic crosslinks occurs to form cyclic sulphides on the rubber hydrocarbon main chains. For the vulcanisation cured at optimum cure time at 140°C, it is estimated there are at least thirty-five accelerator pendent groups and about 100 cyclic sulphides per hundred chemical crosslinks 'grafted' on the main chains. This network structural composition could account for the good strength properties over a wide range of temperatures, including good heat ageing, hysteresis and creep properties (CHAN, *et al.*, 1974).

Resistance to Thermal Oxidation Ageing

The FSEV vulcanisate, with low concentration of polysulphidic crosslinks, displays bet-

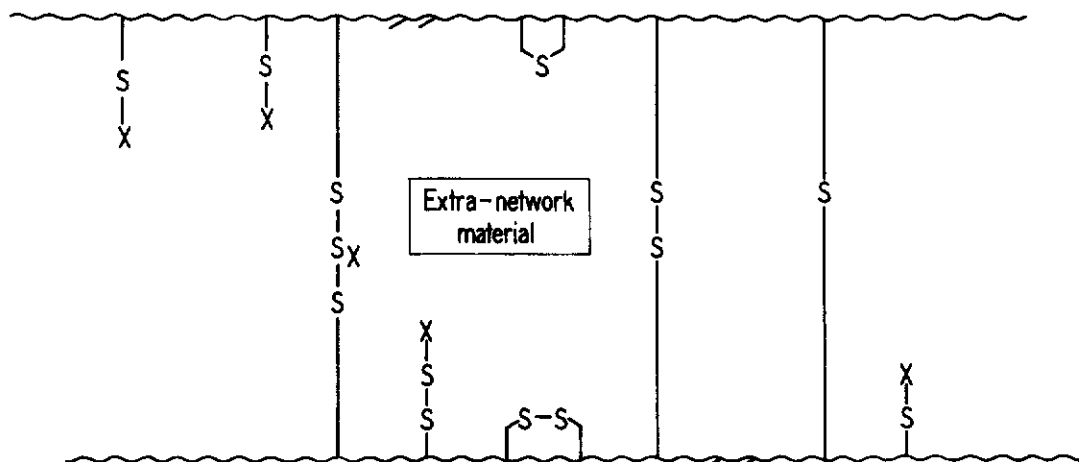


Figure 2. Structural features of a NR accelerated sulphur vulcanisate network: Polysulphidic crosslinks (R-S-S_x-S-R, $x \geq 1$), disulphidic crosslinks (R-S-S-R), monosulphidic crosslinks (R-S-R), cyclic sulphide (R-R), pendent accelerator group (R-S-X, X = accelerator fragment), Diene

ter thermal ageing properties than the conventional system. As in the case of an EV system during vulcanisation, zinc dibutyl dithiocarbamate ($ZD_B C$) is formed *in situ* from the TBTD accelerator present in the curatives. $ZD_B C$ and zinc mercaptobenzothiazole (ZMBT) are well known antioxidants (SKINNER AND WATSON, 1967). Hence, the presence of $ZD_B C$ in the rubber matrix substantially enhances the heat ageing resistance of the FSEV system rubbers.

In spite of the generation of $ZD_B C$ during vulcanisation, it is necessary to add antioxidants to give sufficient protection to the vulcanisates under actual service conditions. Among the commercial antioxidants evaluated in a 50 phr FEF black-filled rubber, there are some differences in protection efficiency in thermal oxidative ageing. For the antioxidants evaluated, both retention of tensile strength and that of breaking elongation of rubber are of smaller magnitude after seven days of oven ageing at 100°C (Table 1). A closer examination showed that the addition of a ketone-amine condensate antioxidant (e.g. Flectol H or Nonox BL) had a slight advantage, possibly due to a combination of zinc dibutylthiocarbamate and the condensate being a more effective antioxidant. A similar report of enhanced antioxidant effect was made in the case of an EV system (SKINNER AND WATSON, 1967).

EFFECT OF CARBON BLACK

The *ad hoc* studies of the black-filled FSEV systems for engineering applications have shown that the system can be compounded, fabricated (ELLOIT, 1974) and even used in high temperature injection moulding. Its reproducibility, precision and low rejection rate of products are recorded (WHEELANS, 1974). Here, a more systematic evaluation is made on the effect of carbon black on the FSEV vulcanisate properties. The mixes contain 10 phr to 100 phr of carbon black (equivalent to volume percent loading from 5 to 32).

Mixing was conducted in a OOC Banbury at 80 rpm with all the curatives added *in situ*. The addition of sulphur and accelerators was made with the Banbury temperature between 100°C–110°C and the mix was dumped when the temperature reached 140°C. The whole mixing cycle was approximately 4 min for lower concentrations of black (< 75 phr) and 6 min for higher concentrations (> 75 phr). For the higher concentrations, an 'upside down' mixing technique was used to give better dispersion of carbon black. The FSEV system is also amenable to single stage mixing with considerable savings in processing cost and time.

Hardness and Modulus

Figures 3 and 4 may be useful guidelines for the selection of a compound of suitable hardness or modulus in a particular application. They show the general reinforcing effect of various carbon black types and the relationships of these properties in the rubber. For a chosen type of carbon black, the hardness or modulus can be achieved by the appropriate choice of the level of concentration of the filler. The data provided would be a good guide to decide on replacement of one type of carbon black by another if hardness or modulus is an important criterion. The results also show the relative reinforcing effect of carbon black types. For the same range of particle sizes, the reinforcement increases progressively in the order: thermal black < furnace black < channel black.

Dunlop Resilience

Figure 5 shows a sigmoidal curve when resilience is plotted against hardness. Resilience generally decreases with increase in hardness and all data fall within a narrow band. There is a close similarity in the performance of the blacks (Figure 5). Marginal differences are observed at different degrees of hardness. At lower hardness (38-43 IRHD) furnace black and channel

TABLE 1. EFFECT OF ANTIDEGRADENTS ON THE TECHNOLOGICAL PROPERTIES OF NR-FSEV VULCANISATES

Antidegradant	Nil	Nonox ON	Nonox BL	Monox DPPD	Nonox ZA	Flectol H	Santoflex IP	OUP	Nonox WSL	BHT
Mooney viscosity	79.5	78.5	83.0	87.5	81	80.5	81.5	79	79	77.5
<i>Vulcanisate properties</i>										
M 100 MN/m ²	3.9	4.0	4.6	4.5	4.4	3.4	3.5	4.0	4.3	4.3
M 300 MN/m ²	16.9	15.1	16.1	16.1	16.4	15.0	15.8	15.6	15.7	16.3
Tensile strength MN/m ²	21.0	24.1	22.0	21.9	24.1	22.7	24.5	22.8	23.8	22.9
Elongation at break (%)	360	440	380	400	420	420	430	410	410	380
Hardness (IRHD)	63	65	66.5	67	66	66	66	65	66	66
Dunlop resilience @ 20°C (%)	73	71	71	66	70	69	70	71	73	72
Flexing to 'C' grade (kilo cycles)		15	24.0	20	22.5	15	22.5	20	20	17.2
<i>Heat ageing 7 days/70°C</i>										
TS retention (%)	82	91	102	103	93	98	94	98	89	88
EB retention (%)	86	89	96	98	95	93	93	98	90	97
<i>Heating ageing 7 days/100°C</i>										
TS retention (%)	60	66	79	73	70	72	73	61	55	55
EB retention (%)	73	80	86	90	86	79	79	90	83	87
<i>Compression set (%)</i>										
72 h/20°C	4.0	5.3	4.4	4.7	5.4	5.3	3.9	3.7	3.2	4.7
7 days/70°C	16.9	16.9	19.4	20.7	18.7	19.9	20.0	18.9	18.4	19.8
7 days/100°C	44.5	54.0	51.4	50.3	53.7	53.2	55.0	51.0	53.0	52.4

Basic Formula: DPNR 100; ZnO 5.0; S 0.8; TBTD 0.8; MOR 1.96; Zinc 2-ethyl hexanoate 1.0; Pine Tar 5.0;
FEF black 50; Antidegradant 2.0. Cured at 140°C for 90 minutes.

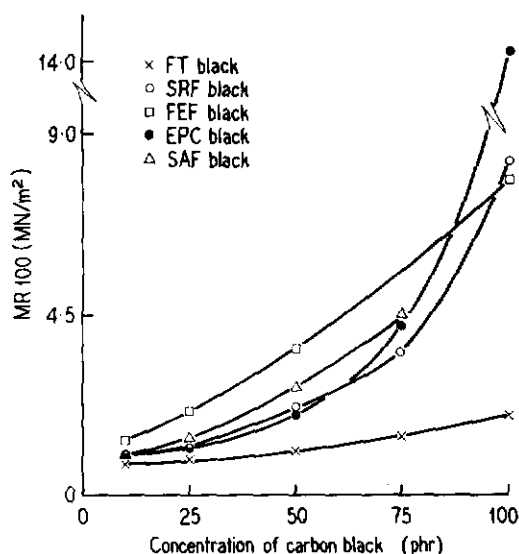


Figure 3. Effect of concentration of carbon black on the relaxed modulus (MR 100) at 100% strain at 20°C.

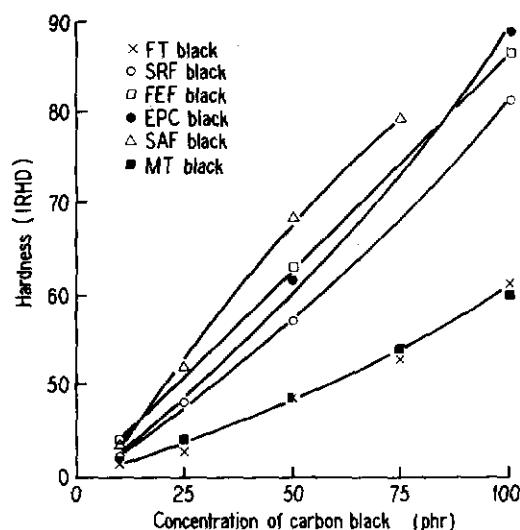


Figure 4. Effect of concentration of carbon black on hardness at 20°C.

black tend to show relatively higher resilience. At the medium range hardness (55-62 IRHD) thermal black seems to show better resilience.

Tensile Strength

The FSEV gum-vulcanisate suffers slight deficiency in the strength properties because of its lack of polysulphidic crosslinks (SKINNER AND WATSON, 1967). However, the black-filled rubbers are as good as those black-filled conventionally cured rubbers. The addition of carbon black lowers the elongation at break, while the tensile strength increases and passes through an optimum. The results are shown in Figure 6. Except for EPC and SRF, the optimum tensile strengths are achieved in the hardness range of 46-50 IRHD, corresponding to 18-22 volume percent of the black. Beyond the optima, the tensile strength decreases with further increase in hardness. EPC and SRF blacks exhibit higher reinforcing effect. This is due to their inter-

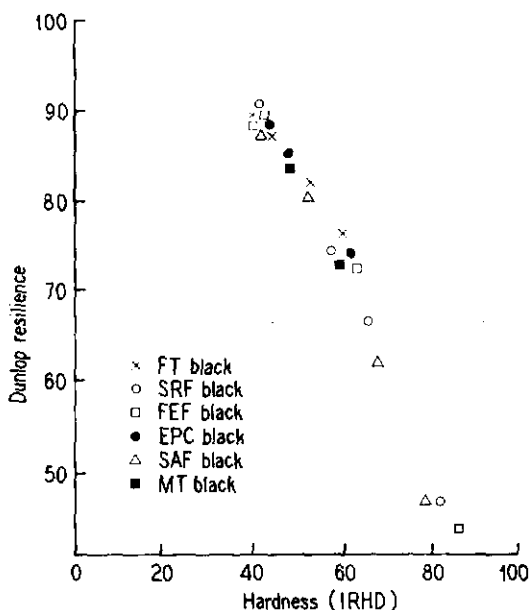


Figure 5. Effect of hardness on Dunlop resilience.

mediate particle size which allows good dispersion because dispersion of filler generally affects strength properties. The optima for

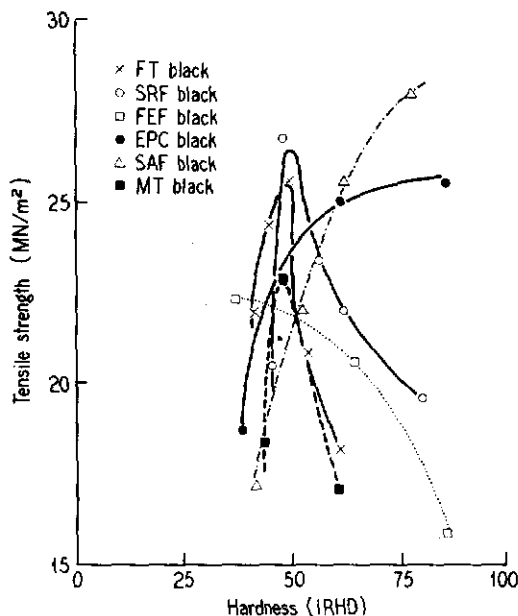


Figure 6. Effect of hardness on the tensile strength at 20°C.

tensile strength for EPC and SRF occur at the higher hardness range of 75-82 IRHD, corresponding to 24-29 volume percent of the black.

Tear Strength

The tear strengths of the FSEV rubbers are shown in Figure 7. They are relatively low when compared with those of a conventional system. The general trend is similar to that of tensile strength. The rubbers of lower hardness (containing lower concentration of filler) show 'smooth' tear pattern, and harder rubbers tend to give 'stick-slip' or 'knotty' tear (GREENSMITH AND THOMAS, 1956). The optimum tear strength has been shown to correlate well with the particle size of the carbon black. For example, MT and FT blacks, having the largest volume factor, hence largest particle sizes, show poorest tear strength, while EPC black of smaller particle size is superior in this respect.

Compression Set

The compression set was measured at 25% strain conditioned for 72 h at 20°C (72 h/20°C) and seven days/70°C. The results are shown in Figure 8. The set increases with increase in the filler concentration, but it falls within a narrow band for a given concentration of all blacks. However, the overall results show that they are lower than those of the corresponding black-filled rubber of the conventional system for the same loading of the filler. Hence, the compression set depends mainly on the chemical network structural composition, but is independent of the black types, including particle size and structure.

Properties Pertaining to Engineering Applications

Essential general requirements for a rubber vulcanisate to be an engineering material are (i) high precision and reproducibility of elastic behavior (GENT, 1962; SMITH, 1973), (ii) low creep or stress relaxation and (iii) curing and processing characteristics of its mix. These alone are sufficient to ensure a high rate of production in the manufacture of

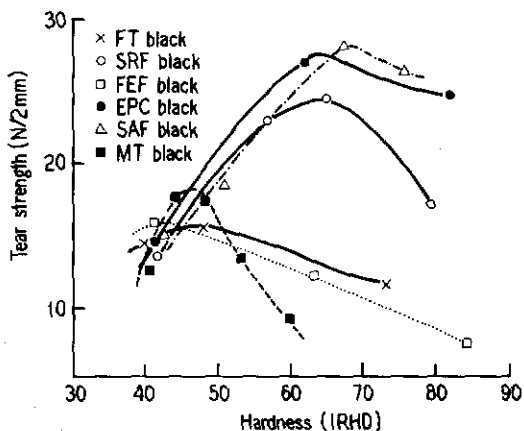


Figure 7. Effect of hardness on the tear strength at 20°C.

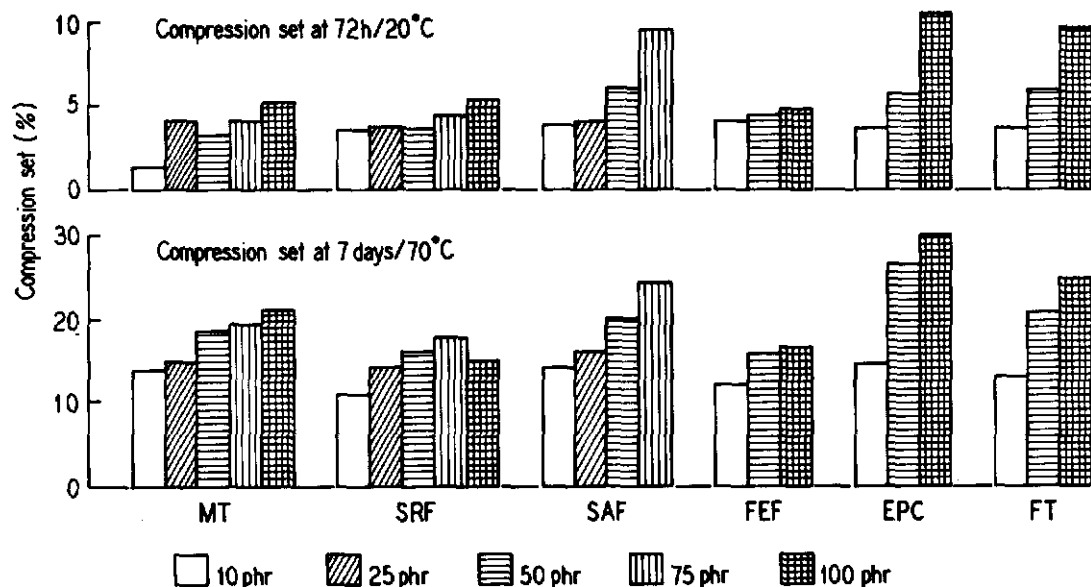


Figure 8. Effect of concentration of carbon black on the compression set.

a rubber component. The use of DPNR coupled with the FSEV system satisfies most of the above requirements. The high degree of precision is shown in Table 2. Compared with other curing systems, its variations in modulus and stored energy (CHAN, 1974) are the smallest. The reproducibility of physical properties is high. Essentially, its network structural features and composition (CHAN, 1974) suffice mechanistic conditions of strength (CHAN AND SMITH, 1974) to have overall strength properties over a wide range of temperature from -40°C to 140°C (CHAN, 1974; CHAN *et al.*, 1974).

Apart from strength properties and high precision in modulus, its stress relaxation rate is lowest amongst known curing systems (HOLLEY, 1973). The rates of stress relaxation for various black-filled DPNR vulcanisates are shown in Table 3. The rate is dependent on the black types and its concentration in the mix. The furnace-processed black have lower relaxation rates than those of the thermal blacks. The medium thermal

TABLE 2. HIGH PRECISION AND REPRODUCIBILITY OF MODULUS (MR 100) IN MN/m^2

Conc. of black phr	MT	FT	FEF	SRF	SAF
25	1.00 ± 0.05	1.03 ± 0.03	1.60 ± 0.07	1.30 ± 0.04	1.35 ± 0.06
50	1.30 ± 0.04	1.25 ± 0.08	3.27 ± 0.15	2.53 ± 0.10	2.72 ± 0.12

TABLE 3. EFFECT OF CARBON BLACK ON STRESS RELAXATION (PERCENT PER DECADE) OF THE FSEV SYSTEM @ 100% STRAIN

Conc. of black phr	Black type				
	MT	FT	FEF	SRF	SAF
10	1.55	1.98	1.07	1.05	0.89
25	1.44	-	-	-	1.78
50	3.07	2.30	2.09	2.05	3.26
70	3.27	-	-	-	3.80
100	6.70	4.30	3.55	5.54	4.90

black by far shows poor or high rate of relaxation, while FEF and SRF blacks show the best relaxation property in the series of investigation.

CONCLUSION

These studies show that rubbers cured with FSEV system, gum-stock or black-filled, have good heat ageing, strength and set properties and are suitable for critical applications particularly in engineering.

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REFERENCES

- BATEMAN, L., CUNEEN, J I MOORE, C G, MULLINS, L AND THOMAS, A G (1963) Correlation of vulcanisate structure and properties *The Chemistry and Physics of Rubber-like Substances and Properties* (Bateman, L ed) p 715 London Maclaren and Sons Ltd
- CAMPBELL D S (1969) Structural characterisation of vulcanisate Pt 10 Thiol disulphide interchange for cleaving disulphide crosslinks in NR vulcanisates *J Appl. Polymer Sci.* 13, 1201
- CAMPBELL, D S (1970) Structural characterisation of vulcanisates Pt 11 Network-bound accelerator residues *J Appl. Polym. Sci.* 14, 1409
- CHAN, B L (1974) The influence of polysulphidic crosslinks on the strength properties of NR gum-vulcanisates *Ph D Thesis* C N A A (U K)
- CHAN, B L, ELLOIT, D J, HOLLEY, M AND SMITH, J F (1974) The influence of curing systems on the properties of NR *J Polym. Sci. Symp. No.* 48, 61
- CHAN, B.L AND SMITH, J F (1974) Unpublished data. Malaysian Rubber Producers Research Association
- ELLOIT, D J (1974) Unpublished report Malaysian Rubber Producers Research Association
- GENT, A N (1962) Relaxation process in vulcanized rubber Part I. Relation among stress relaxation, creep, recovery and hysteresis *J Appl. Polym. Sci.* 6(22), 433
- GREENSMITH, H W AND THOMAS, A.G (1956) Rupture of rubber Pt 4 Tear properties of vulcanisates containing carbon black. *J Polym. Sci.*, 21, 175
- HOLLEY, M. (1973) Unpublished report Malaysian Rubber Producers Research Association
- HOLLEY, M AND SMITH, J F (1973) New principles in the compounding of NR for improved hysteretic properties *IRC 1973 Prague*
- MOORE, C.G AND TREGO, B R (1964) Structural characterisation of vulcanisates Pt. 4 Use of tri-phenylphosphine and sodium di-n-butyl phosphite to determine the structures of sulphur linkages in NR, *cis* 1,4-polyisoprene and ethylene-propylene rubber vulcanisate networks *J Appl. Polymer Sci.*, 8, 1957.
- PARK C R, PARKER, D K AND CHAPMAN, D.A (1972) Pendent accelerator groups in the ageing of rubber *Rubb. Chem. Techn.*, 45(2), 467
- PORTER, M AND HIGGINS, G M.C. (1963) The MBT-accelerated sulphuration of 2, 6 dimethylocta-2,6 diene Unpublished work Natural Rubber Producers Research Association
- SAVILLE, B AND WATSON, A A (1967) Structural characterisation of sulphur-vulcanised rubber network *Rubb. Chem. Techn.*, 400, 100.
- SKINNER, T D AND WATSON, A A. (1967) EV Systems for NR Pt 1. RUSSEL, R.M., SKINNER, T.D. AND WATSON, A A EV Systems for NR Pt 2 *Rubber Age, November and December Issues.*
- SMITH, J F (1973) NR compounds for low creep and improved dynamic performance *Proc MRPRA 3rd Rubb. Engng Conf 1973* (Lindley, P.B. and Rodway, H.G ed)
- WHEELANS, M A (1974) Unpublished report. Malaysian Rubber Producers Research Association.

APPENDIX

I *Types of carbon black used*

Sterling MT	United N550 (FEF)
Acarb SRF	Spheran 9 (EPC)
United N110 (SAF)	Sterling FT
All blacks have medium structure	

II *Compound formulation*

DPNR	100
ZnO	5.0
Zinc Ethylhexanoate (Manomet 22)	1.0
Sulphur	0.8
MOR	1.96
TBUT	0.8
Carbon black	variable
Cured at 150°C for 60 min	

III *Volume fraction of carbon black*

Consider V_i be the volumes of rubber, zinc oxide, filler, etc. and $i = 1, 2, 3, \dots$ depending on the total number of rubber additives. Then the volume fraction is defined here as V_b for carbon black.

$$V_b = V_b / \sum V_i$$

IV *Rubber chemicals*

Zinc oxide
 MC sulphur
 TBUT (Tetrabutyl thiuram disulphide) Robinson Co. Ltd
 MOR Santocure (Monsanto)
 Zinc 2-ethyl hexanoate (Manomet 22) Robinson Co. Ltd
 Pine tar
 FEF black (United N550)

V *Antidegradants*

Trade name

Chemical name

Nonox DN	Phenyl-beta-naphthalylamine
Nonox BL	Diphenylamine-acetone condensate
Nonox DPPD	NN' diphenyl-p-phenylene diamine
Nonox ZA	N-isopropyl N' phenyl-p-phenylene diamine
Flectol H	Poly-2,2,4 trimethyl 1,2 dihydroquinoline
Santoflex IP	N -isopropyl N' phenyl-p-phenylene diamine
UOP 88	SymNN'Di-(3,5 methylheptyl)-p-phenylene diamine
Nonox WSL	1-methylcyclohexyl derivative of xylenols
BHT	2,6 tert-butyl p-cresol
-	without antidegradant

VI *Test methods*

Tensile strength

BS 903 : Pt A2

Hardness

BS 903 : Pt A26 using normal test method

Compression set

BS 903 : Pt A6. 25% strain type 1 test
piece

Resilience

BS 903 : Pt A8

MR 100

BS 1673 : Pt 4 para 4.62